Indian J. Phys. **79(4)**, 425-427 (2005)

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AN INTERNATIONAL JOURNAL

IJP

Electrical conductivity measurements on pure and impurity-added calcium tartrate tetrahydrate single crystals

X Sahaya Shajan[1] and C K Mahadevan*

Physics Research Centre, S T Hindu College, Nagercoil-629 002, Tamilnadu, India

[1]Department of Physics, Sivanthi Aditanar College, Pillayarpuram-629 501, Tamilnadu, India

E mail : ma sancharnet.in

Received 22 June 2004, accepted 11 February 2005

Abstract : Electrical conductivity measurements were carried out on polycrystalline samples of pure and impurity-added calcium tartrate tetrahydrate (CTT) crystals grown by the gel method. The conductivities (both a.c. and d.c.) were measured from room temperature to 75°C in the frequency range 10^2 to 10^4 Hz. The present study shows that the conductivity in pure and impurity-added CTT, increases with the increase in temperature.

Keywords : Calcium tartrate tetrahydrate, electrical properties, a.c conductivity, d.c conductivity, impedance spectroscopy

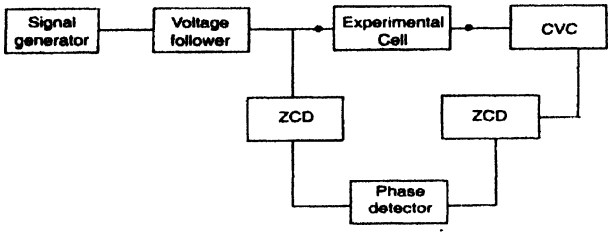
PACS Nos. : 72.20.-i, 72.80.Sk, 81 10.Dn

Tartrate crystals are having physical properties of considerable interest. Some crystals of this family are ferroelectric [1–3], some others are piezoelectric [4] and quite a few of them have been used for controlling laser emission [5]. Calcium tartrate tetrahydrate (CTT) crystals are found to be orthorhombic with lattice parameters : a = 9.24 ± 0.02 Å, b = 10.63 ± 0.02 Å and c = 9.66 ± 0.02 Å and space group $P2_12_12_1$ [6]. Growth and characterization of CTT crystals, both pure and doped, have invited the attention of several researchers in the recent years [7–9]. However, literature apparently shows very little work done on the electrical conduction of pure and impurity-added CTT crystals [10]. Therefore, in the present study, we venture to carry out the investigations on electrical conductivity in association with the thermal variation in order to understand the mechanism of charge transport in this material, CTT. In the present investigation, we attempted to study the effect of addition of isovalent impurity (Sr^{2+}) (at various concentrations) on the electrical conductivity of CTT crystals at various temperatures ranging from room temperature to 75°C in the frequency range 10^2 to 10^4 Hz. We report, herein, the results obtained.

The straight tube diffusion method was employed to grow calcium tartrate tetrahydrate single crystals in the gel medium. 0.5 M sodium metasilicate ($Na_2SiO_3.9H_2O$) was titrated with 0.5 M tartaric acid till the mixture attains the pH 4.2. This gelling mixture was allowed to set in glass tubes of length 200 mm and diameter 25 mm. The gel was set in about 48 hours. After a gel aging of one day, the supernatant solution was added over the set gel. The supernatant solution was a mixture of 0.5 M calcium formate and 85% formic acid so that the pH of the solution was between 1 and 2. This method was found to be better than the conventional way of growing CTT crystals from calcium chloride. The details of crystal growth studies are discussed elsewhere [11]. Strontium-added calcium tartrate tetrahydrate crystals were grown in six different impurity concentrations, *viz.* 0.4, 0.8, 1.2, 1.6, 2.0 and 10 mole%. Strontium chloride was mixed with the supernatant solution and allowed to diffuse into the gel medium containing tartaric acid.

*Corresponding Author

The morphology of the grown crystals was not in favour of preparing well-shaped sample crystals for electrical measurements. Hence, the grown crystals were powdered and made into pellets (polycrystalline) of diameter 10 mm and thickness 3 mm. The pellets were prepared using a 100 tonne hydraulic press ('LYNX', Lawrence & Mayo, India). The pressure applied was about four tonnes. The surfaces of the pellet in contact with the electrodes were coated with good quality graphite paste. Now, the pellet was placed between the electrodes of the experimental cell. The experimental cell consists of two electrodes made up of stainless steel coated with silver and having diameter same as the pellet and kept parallel to each other similar to a parallel plate capacitor. This experimental cell was electrically shielded and was placed in an electric oven for temperature variation.



CVC – Current to voltage converter; ZCD – zero crossing detector

Figure 1. Block diagram of the experimental set-up used for impedance mesurements.

An electronic circuit was fabricated similar to the one already reported in the literature [12]. The block diagram of the circuit used is illustrated in Figure 1. Knowing the phase angle (ϕ) from the output of the phase detector, the real value of the complex impedance was determined using the relation

$$Z' = |Z| \cos\phi, \quad (1)$$

where $|Z| = R_f / A$, R_f is the feedback resistor used in the current to voltage converter (of the order of 100 megohms) and A is the gain which can be calculated from the input and output voltages of the experimental cell with sample.

After knowing the real value of impedance, the real part of conductivity σ_{ac} was determined using the relation,

$$\sigma_{ac} = t/(Z' a), \quad (2)$$

where t is the thickness of the sample, a is the area of the pellet in contact with the electrodes.

The real part of conductivity σ_{ac} was measured in the frequency range 10^2 to 10^4 Hz for temperatures ranging from room temperature to 75°C. A frequency dispersion analysis was carried out by plotting the real part of conductivity (σ_{ac}) of pure and impurity-added CTT crystals as a function of frequency for different temperatures. A best-fit line was drawn using the principles of least squares on these plots and the y-intercept on $f = 0$ axis was determined. This y-intercept gives the conductivity of the sample at zero frequency, *i.e.* the d.c. conductivity (σ_{dc}).

Variation of σ_{ac} with temperature for frequencies 10^2, 10^3 and 10^4 Hz are shown in Figure 2 and the variation of σ_{dc} with temperature is shown in Figure 3. The effect of impurity concentration on the a.c. conductivity (σ_{ac}) for different frequencies at 40°C is illustrated in Figure 4. σ_{ac} value increases with the increase in frequency from 10^2 to 10^4 Hz. However, there is no significant difference observed between σ_{ac} for 10^2 Hz and σ_{dc} values.

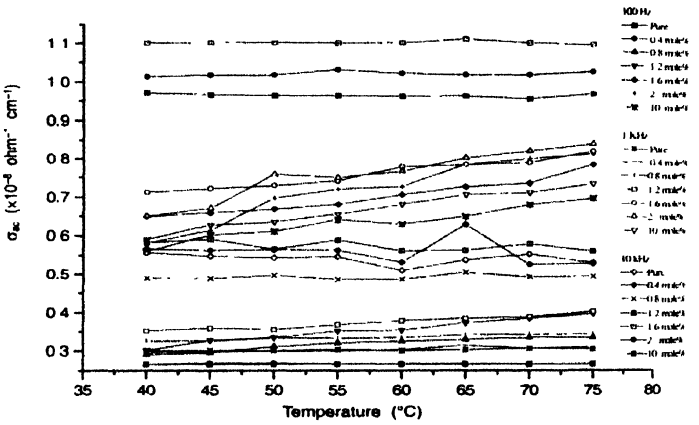


Figure 2. Variation of σ_{ac} with temperature.

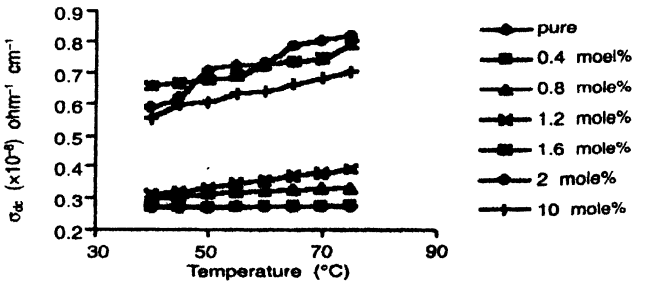


Figure 3. Variation of σ_{dc} with temperature.

It can be seen that the σ_{ac} and σ_{dc} values increase due to impurity addition (except for 0.8 mole% impurity-added CTT for the frequency 10^4 Hz). For impurity-added CTT with impurity concentrations ranging from 0.4 to 1.2 mole%, σ_{ac} and σ_{dc} values are found to be closer to that of the pure one and remain more or less

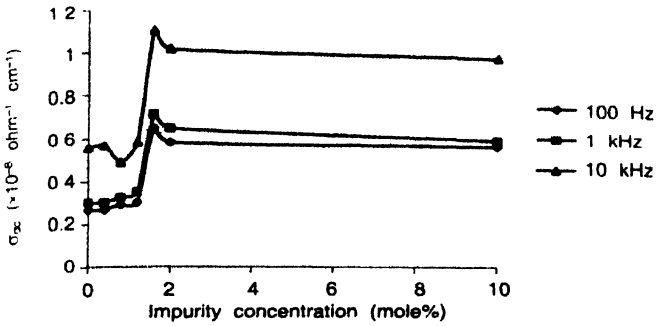


Figure 4. Variation of σ_{ac} with impurity concentration at 40°C.

constant in the temperature region considered in the present study (40 to 75°C). The curves are not even separated for σ_{ac} for frequencies 10^2 and 10^3 Hz and σ_{dc} in the case of pure and 0.4 mole% impurity-added CTT. It may be due to the fact that in this region, the impurity concentration is more in the crystal than that was actually added in the solution and impurity atoms entered into the crystal, are expected to replace the calcium ions. Therefore, excess charge carriers in the form of ions, protons, *etc.* may not be available for conduction in this region. The impurity concentrations obtained using atomic absorption spectroscopic analysis for the grown crystals are given in Table 1. For impurity concentrations ranging from 1.6 to 10 mole%, it can be seen that the conductivity values have increased. This may be due to some increase in the number of defects in the crystal. The conductivity values obtained in the study for CTT are of the same order with that available in the literature (10^{-7} to 10^{-8} ohm^{-1} cm^{-1}) [10].

Table 1. Impurity concentration in the grown crystals obtained using AAS.

Impurity concentration added (mole%)	Impurity concentration in the crystal (mole%)
0.4	1.740
0.8	1.600
1.2	1.636
1.6	2.770
2.0	2.740
10.0	4.660

In the present study, we have used pure and impurity-added CTT pellets for conductivity studies. As pellets are polycrystalline, grain boundaries are present and therefore when an electric field is applied some of the charge carriers will be trapped at grain boundaries and give rise to interfacial polarization resulting in lower conductivity. As far as CTT crystals are concerned, no significant difference in conductivity was observed for pellets and crystals. Conductivity measurements were done for pure CTT crystal and we found that there was only a slight increase in the value of conductivity but the order ($\times 10^{-8}$ ohm^{-1} cm^{-1}) remained the same. Torres [13] has also found similar observations on these crystals.

The tartrate ions in the system considered in the present study, are likely to have a restricted rotation. This rotation of the tartrate ion is closely related to the hydrogen bonding system. The conduction mechanism in tartrate crystals may be explained by the rotation of the tartrate ion [10]. When the temperature of the crystal is increased there is a possibility of weakening of the hydrogen bonding system due to this rotation of the tartrate ion. This results in an enhanced conduction in these materials. In the present study, no remarkable increase in the conductivity is observed in the temperature range 40 to 75°C. This shows that within this temperature range, there is no rotation of the tartrate ion taking place in CTT and hence no weakening of the hydrogen bonding system occurs.

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